DIFFUSION KINETICS IN THE REACTION OF CORUNDUM REFRACTORIES WITH A GLASS MELT

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Diffusion kinetics in contact of electromelted corundum refractories with the glass melt was investigated. The diffusion coefficients of Al^{3+} and their temperature dependence were determined. The basic tenets of diffusion kinetics in service of refractories in glass furnaces and feeder channels are examined.

Electromelted refractories are predominantly used in the glass industry. Corundum refractory articles are highly recommended in lining for the feeder channels of glass molding machines. Their high stability at the temperatures of preparation of the glass melt for molding ensures a long lifetime and prevents the appearance of glass flaws in the finished products.

At the same time, the complex process of the reaction of refractories with the glass melt, including surface phenomena, chemical reactions, transfer phenomena (diffusion, viscous flow, heat transfer) and other factors has been insufficiently investigated. This especially concerns diffusion phenomena; the information on the diffusion coefficients of different ions is limited and primarily concerns diffusion of Na^+ ions at low temperatures [1].

Experimental methods. Samples of electromelted corundum refractories were used for the study (mass content, %): 1) 100 Al_2O_3; 2) 96.50 Al_2O_3, 2.65 SiO_2, 0.41 Na_2O, 0.05 K_2O, 0.12 Fe_2O_3, 0.27 other oxides. Composition of the glass (%): 75 SiO_2, 10 CaO, 15 Na_2O. The experiments consisted of melting glasses of the given composition, obtaining data on the viscosity and density of the glasses with consideration of dissolution of the refractories, determination of the concentration ratios in dissolution, the diffusion characteristics, etc.

To study corrosion of the refractories in the glass melt, different static and dynamic methods were used [2] which allowed obtaining a comprehensive evaluation of the glass stability of the refractory materials without separating the individual constituents of the process. The methods are relatively graphic in conducting comparative tests of samples of refractories using the same experimental setup. Comparable results cannot be obtained on different setups, so that theoretically substantiated methods of diffusion kinetics in moving media for different conditions were used to study the diffusion characteristics in reaction of the refractories with the glass melt.

Such methods are the rotating disk method (sample of the investigated refractory) ensuring the perpendicularity of diffusion flow to the surface [3, 4]. When this method is used, the following picture of movement of the liquid is observed. Ascending flow to the disk is observed at a sufficient distance from the rotating disk, and in the layers immediately adjacent to the disk, the liquid acquires rotational motion, and the angular velocity increases in approaching the disk, to a value equal to the angular velocity of the disk itself. The rotating disk has an important feature that ensures equal accessibility of the surface with respect to diffusion, which is very important for real solids whose surface is usually not homogeneous. In addition, the thickness of the boundary layers in this case will have a constant value over the entire surface.

The analysis of the hydrodynamics of movement of a liquid given in [3] allowed obtaining an equation for calculating the rate of dissolution of solid samples with consideration of the diffusion coefficients:

$$j = 0.62 D^{2/3}\, \nu^{-1/6}\, (c_s - c)\, \omega^{1/2},$$

where D is the diffusion coefficient; ν is the kinematic viscosity; $(c_s - c)$ is the difference in the saturation concentrations at a sufficient distance from the rotating sample; ω is the angular velocity of rotation of the sample.

The high-temperature versions of the rotating sample method were used by P. M. Shurygin and other scientists in investigating diffusion kinetics for metallurgical melts (slags, salts) [5, 6]. The research of M. Trukhlarova and O. Veprek (1969 – 1970) should also be noted, as they used the rotating quartz cylinder method in studying diffusion of SiO_2 in sodium–calcium–silicate glass [1]. B. Ya. Ten [7] used the method of calculating the diffusion coefficient of SiO_2 with the kinetic curves of dissolution of silica grains.

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In conducting our experiments, the samples were attached in the corresponding holder and rotated with low angular velocities, which excluded turbulent modes in consideration of the high viscosity of the melts. The diffusion coefficients were calculated with the experimental data using the above equation. The saturation concentration (solubility of Al_2O_3 in the glass melt) was determined with the full $Na_2O - CaO - Al_2O_3 - SiO_2$ diagram.

Chemical reaction of refractories with the glass melt. The reaction of a glass melt with a refractory, including the diffusion kinetics, is complex and requires special studies with analysis of an important amount of experimental data. Nevertheless, based on the available data, it is possible to hypothesize a two-stage model of the reaction with consideration of structural factors and diffusion kinetics [4, 8].

On contact of the glass melt with the refractories, the refractory first reacts with the most active alkali ions in the glass melt. The scheme of the reaction can be represented as follows. On "attack" of the alkali ions on the crystal lattice of the refractory material, it is destroyed with subsequent migration of the constituent elements into the glass melt. In the case of corundum refractories, Al^{3+} ions and oxygen are formed, and for oxygen, bridge ions are converted into free nonbridge ions:

$$2O^0 \rightarrow O^{2-} + O^-.$$
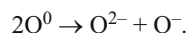
These ions diffuse into the glass melt and participate in formation of coordination polyhedrons. It is necessary to keep in mind here coupling of the flows of charged particles. Departing from conditions of electroneutrality, movement of ions of the same sign should be accompanied by movement of ions of the opposite sign. In this case, the diffusion kinetics will change as a function of the chemical and structural changes in the glass in the contact zone.

In the initial period of the reaction, the driving force of diffusion of the Al^{3+} ion is much greater than for oxygen ions due to the concentration ratios; on the contact boundary, the concentration of Al^{3+} is maximum and equal to zero in the glass, while the difference in the concentrations of oxygen ions is insignificant (in the glass, the concentration of active oxygen ions is determined by the Na_2O and CaO content). In consideration of the size of the Al^{3+} (0.57 Å) and oxygen ions (1.36 Å), the driving force of diffusion of Al^{3+} will be much higher than for oxygen ions.

In migration of the Al^{3+} ion out of a corundum refractory into glass, its coordination number for oxygen changes from 6 to 4. In glass, the Al^{3+} ion, surrounded by four oxygen ions, can isomorphically replace the Si^{4+} ion in silicon–oxygen formations. Highly coherent single silicon–aluminum–oxygen formations arise. This is indicated by the increase in the viscosity and surface (interfacial) tension. As indicated in [8], the state of structural oxygen in the glass-forming melt is determined by the equilibrium conditions:

$$O^0 + O^{2-} \leftrightarrow 2O^-.$$
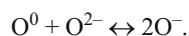
These conditions will change when the O^{2-} and O^- ions arising in decomposition of the crystal lattice of corundum appear. Bridge O^0 ions in the glass-forming melt are already bound with silicon and do not participate in formation of ionic aluminum–oxygen polyhedrons (tetrahedrons), so that the excess of active oxygen ions, predominantly O^-, is used to construct these tetrahedrons. The use of the oxygen ions in the glass for this purpose will approximately continue until the condition $(Na_2O + CaO)/Al_2O_3 = 1$ is satisfied. Furthermore, oxygen ions formed in decomposition of the crystal lattice of the corundum refractory will be used for building aluminum–oxygen tetrahedrons until the saturation concentration of Al_2O_3 is attained in the glass. The driving force of diffusion for oxygen ions should increase due to the important difference in the concentrations of active oxygen ions on the contact boundary and in the glass and should decrease for Al^{3+} because of a decrease in the difference in concentrations. However, the difference in the size of the ions can level out the diffusion characteristics of the ions. The overall rate of the diffusion process will slow, however.

In the contact zone, saturation of the glass melt with Al_2O_3 occurs according to the $Na_2O - CaO - Al_2O_3 - SiO_2$ phase diagram. Applying the composition of the glass used in the diagram and joining it with the Al_2O_3 apices, we obtain the direction of the reaction of the corundum refractory with the glass melt and the compositions of intermediate and crystallized products. As the diagram suggests, these products are mixtures corresponding to minerals of the sodium and calcium feldspar series. Products of the sodium feldspar series are primarily formed due to the higher reactivity of the Na^+ ions and in particular, nepheline and carnegieite:

$$2Al_2O_3 + Na_2O + 2SiO_2 = \underset{\text{nepheline, carnegieite}}{Na_2O \cdot Al_2O_3 \cdot 2SiO_2} + Al_2O_3.$$
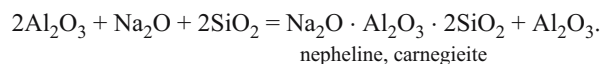
A multitude of small crystals of these compounds is founding the contact zone in the glass, which has also been noted by other investigators [2].

Features of diffusion kinetics. High-temperature reactions of a highly viscous melt with a solid and correspondingly diffusion phenomena are very complex.

Transfer of a substance in a moving liquid is due to two different mechanisms. First, when there is a concentration difference in the liquid, molecular or ionic diffusion arises; second, particles of the substance dissolved in the liquid are entrained by the liquid as it moves and are conveyed along with it. The special processes characterize convective transfer of matter in a liquid.

It should be noted that the substantiated theoretical assumptions of convective transfer were basically elaborated for low-viscosity liquids, and the necessity of studying diffusion kinetics in highly viscous liquids was emphasized in [3, 4], since the experimental data for them are clearly insufficient.

The Reynolds number and diffusion number, which respectively characterize the movement mode and the physico-
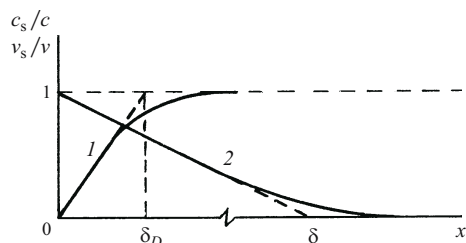
Fig. 1. Character of the change in the concentration of Al_2O_3 (*1*) and rate of melt movement (*2*) in a rotating disk sample in the direction of diffusion flow: v_s) rate of melt movement on the inner boundary of the hydrodynamic layer; v) same for the outer boundary.

chemical properties of the liquid, are the basic parameters of a moving liquid. Movement of a glass melt in glass furnaces is characterized by low values of the Reynolds number and a regime of developed turbulence is difficult to create in general for a highly viscous glass melt. For this reason, the importance of the Prandtl diffusion number increases as one of the basic characteristics of a highly viscous melt:

$$Pr = \nu/D.$$

For glass melts, the Prandtl diffusion number can be equal to $10^8 – 10^{10}$ m^2/sec. Such high values emphasize some features of the diffusion process in highly viscous melts.

For experimental and industrial conditions, the entire volume of a highly viscous melt can arbitrarily be divided into three regions:

the region of the basic volume of the melt in which the concentration of dissolved refractory matter is insignificant in comparison to the saturation concentration; movement of the glass melt in this volume is due to organized convective diffusion (experimental vessel) or production and convective flows (glass furnace);

the region of constant concentration distribution and convective diffusion at a certain distance from the surface of the refractory – the hydrodynamic boundary layer (in the scientific literature, it is also called the "Prandtl layer"); laminar movement occurs here and the viscosity of the melt plays the basic role; in studying the diffusion characteristics by the rotating disk method and low values of the Reynolds number, the thickness of the hydrodynamic layer is commensurate with the radius of the disk [3]; it was noted in [9] that in dissolution of refractories in melted glass and other silicate melts that are highly viscous, not very mobile liquids, relatively thick boundaries layers which can attain 10^{-2} m and more are formed;

the region of a rapid change in concentration and diffusion of directly near the surface of the refractory material – the diffusion layer (also called the "Nernst layer" in the scientific literature); saturation concentrations are attained here; for highly viscous glass melts enriched with high-melting components of the refractories, this layer can be considered strongly bound with the surface of the refractories; the prod-

ucts of dissolution migrate into the bulk of the melt by convective diffusion through the hydrodynamic boundary layer; the products of dissolution go from here into the bulk of the melt by convective diffusion through the hydrodynamic boundary layer; the thickness of the diffusion layer δ_D is small and in agreement with the data in [3, 4], can be approximately determined from the relation:

$$\delta_D = \delta/Pr^{1/3},$$

where δ is the thickness of the hydrodynamic layer.

It follows from this relation that the thickness of the diffusion layer decreases significantly with an increase in the viscosity of the liquid (for glass melts, at a hydrodynamic layer thickness of 10^{-2} m and a Prandtl number of 10^9, the thickness of the diffusion layer will be 10^{-5} m, while the Prandtl number will only be 10^3 and correspondingly, the diffusion layer thickness will be 10^{-3} m for aqueous medium with the same hydrodynamic layer thickness). Similar results were obtained in [10] for the reaction of a glass melt with refractories (with consideration of the assumptions made and experimental conditions).

The generalized dependences of the change in the reported concentration of Al_2O_3 and the rate of movement of the melt in the direction of diffusion flow perpendicular to the surface of the rotating samples (axis *x*) are shown in Fig. 1. The thickness of the diffusion and hydrodynamic layers is determined by the points of intersection of tangents to the curves with the level of limiting values of the concentration and movement rate. These values are attained on the inner and outer boundaries of the hydrodynamic layer. As noted, beyond the limits of the outer boundary of the hydrodynamic layer, the character of movement of the liquid changes, related to the presence of ascending flow to the disk.

The experimental dependences of the rate of dissolution of the disk samples on the angular velocity of rotation and the temperature are shown in Fig. 2. The linear character of the dependence indicates a diffusion mode of dissolution of the refractory samples, i.e., the dissolution rate is not limited by the rate of the chemical reaction, but by removal of the products formed from the reaction zone. The temperature dependence of the diffusion coefficient is shown in Fig. 3. The activation energy of the diffusion process was determined with the experimental data obtained and was 258 kJ/mole. The low values of the diffusion coefficients and high activation energy of the process indicate the elevated resistance of electromelted corundum refractories to sodium–calcium–silicate glass melts.

Simlar experiments were conducted with samples of industrial corundum refractories containing small amounts of silica, sodium, potassium oxides, etc., in addition to Al_2O_3. The content of these oxides increases the thermal stability of the refractories, but their glass stability decreases relatively significantly. This is indicated by the values of the diffusion coefficient of Al^{3+}, whose value increases by more than one
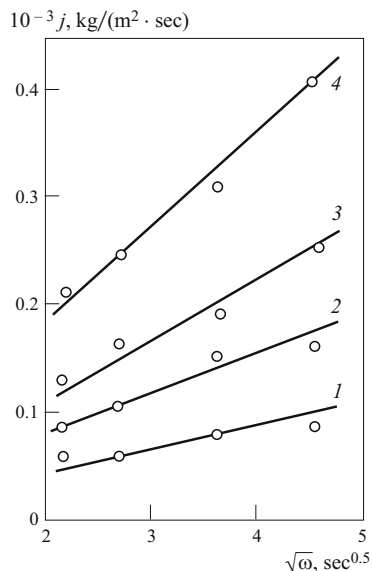
Fig. 2. Rate of dissolution of refractory sample (Al_2O_3) on angular velocity of rotation at temperatures of 1350°C (*1*), 1400°C (*2*), 1450°C (*3*), and 1500°C (*4*).

Fig. 3. Temperature dependence of the diffusion coefficient in dissolution of Al_2O_3 in a glass melt.

Fig. 4. Character of diffusion kinetics in an immobile refractory: *a*) diagram of movement of the melt and velocity distribution in flow of a glass melt in convective diffusion; *b*) character of the change in the concentration of Al_2O_3 (*1*) and rate of melt movement (*2*) in the direction of diffusion flow.
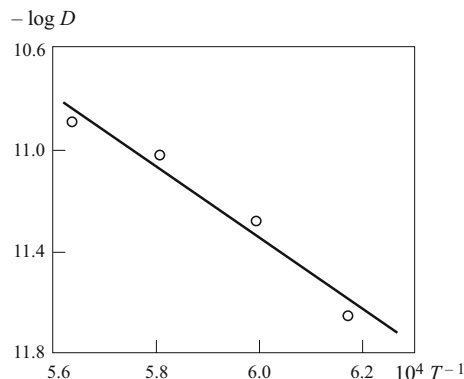
order of magnitude, especially at high temperatures. This is due to the presence of a small amount of glass phase containing alkali oxides. Penetration of Na^+ from the glass into the refractory also takes place over the glass phase.

The increased mobility and reactivity of the sodium ions, especially at high temperatures, create the conditions for destruction of the crystal lattice of the refractory from the inside and significantly increase the diffusion coefficient of Al^{3+}. For this reason, it is best to use electromelted corundum refractories for the feeder pans of glass-forming machines, where the temperature is 150 – 200°C lower than in the melting part of the glass furnace. The comparatively low temperature in the feeders and the related high viscosity of the glass melt decrease the aggressiveness of the melt and the diffusion coefficient of the ions. At the same time, the increase in the rate of movement of the glass melt in the feeder channels causes accelerated removal of the products formed from the zone of the chemical reaction.

Diffusion kinetics in industrial conditions. In consideration of the importance of the corrosion resistance of refractory materials in glass furnaces, the reaction of these materials with the glass melt has been investigated in many studies, most of which have been published [2, 11].

Let us consider some features of diffusion phenomena on contact of the glass melt with the walls of feeder channel pans made of electromelted corundum refractory. Similar phenomena will also take place on contact of the glass melt with the wall blocks of the glass furnace (the character of the diffusion kinetics with consideration of the ZrO_2 content is not examined here).

A diagram of movement of a melt and distribution of the rates in flow of a glass melt moving relative to the immobile refractory wall parallel to axis *y* (production flow) is shown
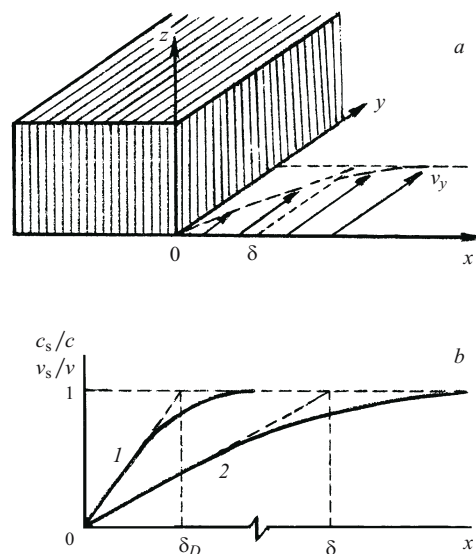
in Fig. 4*a*. The flow rate increases from zero (on the surface of the refractory) to defined values within the limits of the hydrodynamic layer. Diffusion takes place in the direction perpendicular to the direction of movement of flow of the glass melt, i.e., along axis *x*. The basic process of diffusion of ions takes place in the thin diffusion layer and beyond its boundaries, convective diffusion takes place in the hydrodynamic layer.

The generalized dependences of the change in the production concentration and Al_2O_3 and the rate of movement of the glass melt are shown in Fig. 4*b*. In this case, in contrast to the rotating samples, the rate on the surface of the immobile refractory (tank block, feeder walls) is equal to zero.

It should be noted that the phenomena examined are secondary. Formation of a diffusion layer primarily takes place

due to the chemical reaction, concentration gradient, and surface forces, and the character of the change in them is given in [11, 12].

We should also note that in the refractory–glass melt contact zone, the portions of glass melt enriched with Al_2O_3 and poor in Na_2O drop down and new portions of glass melt with a lower Al_2O_3 content or with no Al_2O_3 appear in their place (gravitational convection). The surface forces acting within the boundaries of the diffusion layer significantly affect dissolution of refractories, despite their low intensity. These forces can change the thickness of the diffusion layer. When it decreases, entrainment of dissolved matter (Al_2O_3) from the reaction zone is accelerated due to convective diffusion, corrosion of refractories is intensified, and flaws appear in the glass melt in the form of ripples, stones, etc.

A difference in the size of surface (interphase) strains on the boundary of the diffusion and hydrodynamic layers. A smaller difference decreases the rate of movement of the glass melt in the contact zone and its effect on the diffusion layer by decreasing the corrosion rate of the refractory. This is especially marked in corrosion on the surface of the glass melt and in vertical pit corrosion [11].

The effect of surface and concentration factors in use of chromium oxide refractories in melting green glass colored with Cr_2O_3 (chromium oxides are surface-active components in the glass) is marked. In this case, the difference in the surface (interphase) stresses is insignificant, and the saturation concentration and concentration gradient ($c_s - c$) for Cr_2O_3 will be much smaller than for Al_2O_3. This significantly decreases the corrosion rate of the refractories. The decrease in the diffusion coefficient also causes an increase in the viscosity of the glass melt in the contact zone, which is usually obtained by cooling the corresponding section of the refractory lining, for example, the top row of wall blocks at the level of the surface of the glass melt and the neck blocks. When Bakor refractories are used, the viscosity increases due to combined dissolution of ZrO_2 and Al_2O_3.

The basic factors of diffusion kinetics in the reaction of corundum refractories with the glass melt, including in industrial conditions, were thus revealed. The experimental re-

sults obtained indicate the diffusion character of dissolution of corundum refractories in a glass melt. The diffusion coefficients of Al^{3+} ions determined with the experimental data are $10^{-11} - 10^{-12}$ m^2/sec.

Analysis and consideration of diffusion kinetics factors will increase the efficiency of use of refractories in glass furnaces.

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